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(54) Flexible composite material and process for preparing same.

EP 0 226 420 A2 (57) A flexible composite material comprising a core composed of a blend of a thermoplastic resin fiber and a reinforcing fiber, and a flexible sleeve formed of a thermoplastic resin and surrounding the core. The composite material may be prepared by intermixing a thermoplastic resin fiber and a reinforcing fiber to obtain a core, and then extruding a thermoplastic resin over the core.

## Flexible Composite Material and Process For Preparing Same

This invention relates to a flexible composite material useful for the molding of composite articles.

As composite material containing a reinforcing fiber such as carbon fiber and so on is generally well known composite material prepared by setting a prepreg in the form of a tape or a woven cloth formed by coating a solution of a thermosetting resin or a low-viscosity molten thermosetting resin on a tow or a woven cloth of carbon fibers or covering the tow or the woven cloth with the solution or the low-viscosity molten material. The prepreg is extremely high in adhesion and poor in flexibility so that it has problems with handling and post-processing. A tape of a carbon fiber-containing thermoplastic resin prepared by extruding a carbon fiber tape in which a thermoplastic resin having a high melting point is impregnated is also known; however, the carbon fiber-containing thermoplastic resin tape is in the state of an extremely rigid board so that it may cause difficulties in the formation of woven clothes and moreover it cannot be subjected to drape forming through molds with complex shapes.

In order to overcome drawbacks as described above, there have recently been proposed a continuous fiber tow (European Publication No. 156599A and No. 156600A) which is formed from a tight blend of about 90 % to 30 % by volume of spun fibers of a thermoplastic polymer and about 10 % to 70 % by volume of carbon fibers or non-thermoplastic reinforcing fibers, each based on the total fiber content and a flexible composite material (European Publication No. 133825A) which is formed by covering coarse fiber filaments impregnated by a thermoplastic resin powder with a flexible covering material. The composite materials are suitable for the drape forming through molds with complex shapes in terms of flexibility as compared to known carbon fiber-containing thermoplastic resin tape; however, they have still drawbacks as will be described below.

The former, on the one hand, may cause fuzzes on its surface so that the step of weaving clothes is rendered uneasy. It also leads to the formation of a large number of fuzzes on the resulting woven clothes, thereby causing the difficulty of providing woven clothes of practical value. Furthermore, as carbon fibers are exposed on the surface of the composite material, the fibers are caused to be easily damaged during the handling and fuzzed. Moreover, it has an additional disadvantage that the material properties of resulting molded products are caused to be impaired because the thermo-

plastic resin fibers and the carbon fibers used are exposed in the atmosphere so that air and moisture are allowed to be permeated through the spaces among the fibers.

5 The latter, on the other hand, causes the difficulty of quantitatively determining rates of blends of the reinforcing fibers and the thermoplastic resin powders because the thermoplastic resin powders are caused to adhere to coarse fiber filaments (reinforcing fibers) using a fluidized layer and so on so that the material properties of resulting molded products are not rendered uniform. This causes the problem that the material properties are unstable. In instances where the composite material is employed in the form of shortly cut chips or where it is woven in clothes in such a form, it has the difficulty that the resin powders in the sleeve will be caused to be scattered during cutting so that the quantitative and uniform properties as a composite material may be impaired and working environment will be caused to be worsened. Further, in the production of the composite material, an extremely severe step of producing powdery particles is required so as to define average particle sizes of the powdery particles within a particular range to maintain a stably fluidized state of the fluidized layer. This will cause to increase a cost of production. As the coarse fiber filaments in which the resin powders are impregnated are used, it has the disadvantage because it is hard to tightly bond the coarse fiber filaments to the flexible covering material, leading to the ready permeation in the composite material of air that may cause a decrease in the material properties of the resultant molded products. It also has the problem that the removal of the air from the sleeve is difficult because this will cause to migrate the powdery particles, thus affecting adverse influences on the quantitative and uniform properties of the resultant molded products.

35 The present invention has the objects to provide a flexible composite material, unlike conventional reinforcing filaments-containing composite material, that enables to blend a reinforcing fiber and a thermoplastic resin fiber at a quantitative and uniform rate and to be processed in an extremely favorable manner, leading to the formation of molded articles with superior mechanical properties such as a tensile strength, bending strength and so on and to provide a process for preparing the flexible composite material in an industrially favorable manner.

In accordance with one aspect of the present invention, there is provided a flexible composite material comprising a core composed of a blend of a thermoplastic resin fiber and a reinforcing fiber, and a flexible sleeve formed of a thermoplastic resin and surrounding said core.

In another aspect, the present invention provides a process for preparing a flexible composite material, comprising providing a thermoplastic resin fiber and a reinforcing fiber, intimately blending said thermoplastic resin fiber and said reinforcing fiber, assembling said blended fibers to obtain a core, and extruding a thermoplastic resin over said core to form a thermoplastic resin sleeve surrounding said core.

The flexible composite material according to the present invention is allowed to determine freely and quantitatively rates of blends of the reinforcing fiber and the thermoplastic resin fiber, unlike in the case that a thermoplastic resin in the form of powder is employed, because a blend of the reinforcing fiber and the thermoplastic resin fiber is used as a core material and a flexible sleeve made from a thermoplastic resin is provided around the core material. As the resultant blended fiber bundle is superior in flexibility, quality and uniformity, the flexible composite material according to the present invention can provide molded articles with superior mechanical properties such as a tensile strength, bending strength and so on.

Also the flexible composite material according to the present invention is provided with a flexible sleeve made from the thermoplastic resin around the core material as described above so that it can prevent air or moisture from being permeated into the flexible composite material, thereby enabling to remarkably improve the mechanical properties of the resulting molded articles. The flexible composite material does not cause fuzzing on the surface thereof and no reinforcing fiber is exposed thereon so that the cloth weaving step and handling are rendered easy, thus causing no damage on the reinforcing fiber in the resulting clothes, woven clothes and so on and leading to the extremely good post-processing. The reason why the flexible composite material according to the present invention performs the remarkable results as described above is because it is based on a combination of the factors constructing the present invention that the blended fiber bundle composed of the reinforcing fiber and the thermoplastic resin fiber is used as a core material and that the flexible sleeve made from the thermoplastic resin is provided around the core material.

To the contrary, without such factors, for example, in instances where a thermoplastic resin in the form of powders is employed in the place of the thermoplastic resin fiber, it is difficult to quantitate

a rate of blending the reinforcing fiber and the thermoplastic resin fiber so that a composite material with high quality and uniformity cannot be produced. When such composite material is cut, the powders within the inside are caused to be removed so that the quantitative property is further impaired, thus leading to the worsening of working environment and the rise of production costs. From these drawbacks, such conventional composite materials cannot perform the effects as in the flexible composite material according to the present invention. In instances where the bundle of reinforcing fiber and the thermoplastic resin fiber is not surrounded with a sleeve, the blended fiber bundle is caused to be exposed directly to air so that air is permeated into spaces among the fibers and material properties of resultant molded articles are caused to be decreased, leading to the production of unstable and ununiform molded articles. Since such composite materials may cause a remarkable number of fuzzes and then the reinforcing fiber is caused to be exposed on the surface, the post-processability becomes extremely poor so that the objects of the present invention cannot be achieved.

The flexible composite material according to the present invention will be described in detail with reference to the accompanying drawings, in which:

Fig. 1 is a fragmentary, perspective view, cut away in part, schematically showing flexible composite material according to the present invention; and

Fig. 2 is a diagrammatic illustration of an apparatus suitable for the preparation of the composite material of the present invention.

Referring to Fig. 1, the reference numeral 1 designates a blended fiber bundle or core surrounded by a flexible thermoplastic resin sleeve 2. The blended fiber core 1 is composed of a thermoplastic resin fiber 3 and reinforcing fiber 4. The filaments of the two fibers 3 and 4 are each generally continuous and are substantially uniformly distributed in the plane perpendicular to the axis of the core 1.

The amount of the thermoplastic resin fiber 3 and the reinforcing fiber 4 in the core may vary with the purpose for or the manner of using the flexible composite material and may preferably range from about 1 % to about 89 % by volume and from about 99 % to about 11 % by volume, respectively, based on the total fiber content. If the blending rates of the thermoplastic resin fiber 3 to the reinforcing fiber 4 are below the above range, it is not preferred because molded articles with high quality and uniformity cannot be produced. If they exceed the above range, it is not preferred, too, because the reinforcing effect to be created by the reinforcing fiber cannot be obtained. More prefer-

ably, the amount of the thermoplastic resin fiber 3 is from about 15 % to about 30 % and the amount of the reinforcing fiber 4 is from about 85 % to about 70 %, each based on the total fiber content.

The thickness of the flexible sleeve 2 made from the thermoplastic resin may range preferably from about 5 to about 2,000  $\mu\text{m}$  and, more preferably, from about 10 to about 200  $\mu\text{m}$ . The thickness of the sleeve below about 5  $\mu\text{m}$  is not preferred because the formation of a uniform sleeve is rendered hard. On the other hand, if it exceeds about 2,000  $\mu\text{m}$ , the object of the present invention cannot be performed because a desired flexibility of composite materials cannot be produced.

In the flexible composite material according to the present invention, the denier numbers of the filaments of the thermoplastic resin fiber may range generally from about 0.001 to about 50 per each filament. In order to provide the flexible composite material of higher quality, it is desired that the denier numbers range from about 0.03 to about 1. Although the number of the filaments may conveniently vary with the denier numbers of the filaments, it may range generally from about 5 to about 20,000,000 and, more preferably, from about 10 to about 100,000.

The reinforcing fiber to be used for the present invention may be one having a filament denier number ranging from about 0.05 to about 600 and the number of filaments ranging from about 50 to about 300,000 and preferably having a filament denier number ranging from about 0.25 to about 16 and the number of filaments ranging from about 100 to about 48,000.

The diameters of the thermoplastic resin fiber to be used for the present invention may range generally from about 0.5 to about 60  $\mu\text{m}$  and preferably from about 2 to 11  $\mu\text{m}$ , while the diameters of the reinforcing fiber may range generally from about 3 to about 50  $\mu\text{m}$  and preferably from about 6 to about 30  $\mu\text{m}$ . It is preferred to generally use the thermoplastic resin fiber having a filament size smaller than that of the reinforcing fiber, because the thinner the thermoplastic resin fiber filaments, the greater becomes the number of the filaments and, thus, the uniformity of the fiber blend is improved.

The flexible composite material according to the present invention is superior in mechanical strength when molded in articles because air and moisture are unlikely to permeate therein because the blended fiber bundle 1 composed of the thermoplastic resin fiber 3 and the reinforcing fiber 4 is used as a core material and a flexible sleeve 2 made from the thermoplastic resin is provided over the surface of the core material 1 as described above.

In accordance with the present invention, the blended fiber bundle 1 and the sleeve 2 can be closely bonded to each other when the step of covering the core with the sleeve is performed while keeping the core under vacuum using a deairing pump, as described hereinafter, so that molded articles having superior mechanical strength can be produced. Such a flexible composite material in which the blended filaments bundle 1 is closely bonded to the sleeve 2 is particularly suitable for a filament winding molding material as will be described below and is molded into articles requiring high quality. In the composite material according to the present invention, it may be possible to provide an arbitrary number of annular knots or depressions thereon using a stamping or hot pressing device in order to maintain the close bonding between the sleeve 2 and the blended fiber bundle 1. The composite material of this shape is suitable, for example, in instances where it is used after cutting into chips between each adjacent knots.

The thermoplastic resin fiber to be used for the present invention may be formed of polymers such as polyamides, polyesters, polyethylenes, polypropylenes, polyvinylidene fluorides, polamideimides, polyimides, polyetherimides, polyethersulfones and polyetheretherketones. More specifically, the polyamide may include homopolymers or copolymers such as nylon 66, nylon 6, nylon 12 and nylon 6/66/12 terpolymer. The polyester may include homopolymers or copolymers such as polyethylene terephthalate, polybutylene terephthalate, polyethylene-2,6-naphthalate, polyoxyethoxybenzo-ate and aromatic polyester.

As the reinforcing fiber 4 to be used for the present invention may be employed a carbon fiber, a glass fiber or a polyamide fiber. More specifically, the carbon fibers may be divided basically into two groups according to the difference in the raw material to be used. Of one group is one prepared by carbonizing petroleum pitch or coal tar pitch used as raw materials. Of the other group is one prepared by carbonizing natural or synthetic fibers used as raw materials. Any one of these groups may be employed for the present invention. In instances where the pitch is employed as a raw material, the pitch is prepared so as to be in such a state as being suitable for a spinning material and then converted into fibers, followed by being subjected to infusion and carbonization. For example, the pitch prepared to have softening points ranging from 180 to 300  $^{\circ}\text{C}$  is molten spun at temperatures from 250 to 350  $^{\circ}\text{C}$ , then subjected to infusion at temperatures from 150 to 300  $^{\circ}\text{C}$  using an oxidizing gas and carbonized at temperatures from 800 to 2,500  $^{\circ}\text{C}$ . In instances where fibers are used as raw materials, cellulose or acryl-

ic fibers, particularly acrylonitrile copolymer fibers, are used as raw materials. They are subjected to a heat treatment and then carbonized. Particularly suitable for the present invention are carbon fibers prepared from the pitch.

The thermoplastic resins to be used as a material forming the flexible sleeve 2 according to the present invention may include a polymer such as polyamide, polyester, polyethylene, polypropylene, polyvinylidene fluoride, polyamidimide, polyimide, polyether imide, polyether sulphone or polyetheretherketone. More specifically, the polyamides may include a homopolymer or copolymer such as nylon 66, nylon 6, nylon 12, nylon 6/66/12 terpolymer. The specific polyesters may include polyethylene terephthalate, polybutylene terephthalate, polyethylene-2,6-naphthalate, polyoxyethoxybenzoate or aromatic polyester. The melting points of the thermoplastic resins to be used as the sleeve-forming material are preferably equal to or lower than those of the thermoplastic resin fibers 3.

The processes of the preparation of the flexible composite material will be described more in detail hereinbelow.

The process for preparing the flexible composite material comprises the steps of blending a thermoplastic resin fiber bundle and a reinforcing fiber bundle and then covering the resultant blended fibers with a thermoplastic resin so as to form a sleeve around the blended fiber bundle.

Referring now to Fig. 2, a bundle of a reinforcing fiber 11 and a bundle of a thermoplastic resin fiber 12 wound on bobbins (not shown) are continuously drawn at a constant speed by a Nelson type feed roller 14 through a fiber blending device 13. The fiber blending device 13 may be of any conventional type and is not specifically shown herein. Briefly, the device 13 is composed of air nozzles and an intermixing means. Designated as 23 and 24 are unwinding equipments for controlling the feed of the fibers:

The two different fiber bundles supplied to the blending device 13 are uniformly spread or separated by the aid of dry air blown from the nozzles and then caused to go into contact with each other for intermixing. During the blending, a tension of 2 grams or higher, for example, is arranged to be applied to the fibers 11 and 12. The blended fiber bundle obtained in the blending device 13 is transferred to a sleeve-covering device composed of a thermoplastic resin extruder 18 and a sleeve-covering cross bed 16 and is covered there with the flexible thermoplastic resin supplied to the extruder 18.

The composite material provided with the sleeve is then cooled and solidified by a cooling device 20 followed by the drawing at a constant speed by means of a Nelson type feed roller 21 and the winding by means of a take-up device 22. The reference numerals 15 and 25 denote sizing rollers which are preferably disposed for surface-treating the reinforcing fiber bundle and the blended fiber bundle, respectively, for the purpose of preventing fuzzes from being caused on the bundles and of increasing the tension of the bundles. The sizing agent to be used for the sizing may also serve to function as a converging agent during the formation of the composite material and also as a binder between the reinforcing fiber and the thermoplastic resin fiber during the molding of the composite material.

In accordance with the present invention, in instances where the sizing rollers 15 and 25 are employed, the production efficiency can be increased to a considerably great degree and there can be produced the blended fiber bundle in which the thermoplastic resin fiber is closely bonded to the reinforcing fiber and also the molded articles in which the thermoplastic resin is closely bonded to the reinforcing fiber.

In Fig. 2, the reference numeral 17 designates a deairing pump, and the pump is useful for the production of composite material in which the core 1 (Fig. 1) of the blended filaments bundle is in close contact with the thermoplastic resin sleeve 2 (Fig. 1) and, hence, for the production of molded articles having an extremely small porosity. That is, by connecting the pump 17 to the cross bed 16, the blended fiber bundle is maintained under vacuum so that interstices between the blended fibers and between the fibers and the sleeve may be reduced to provide tight bonding between the fibers and between the core and the sleeve.

Designated as 19 is a stamping or knot forming device, and it is useful for the production of the composite material according to the present invention suitable for being cut into a multiplicity of chips. The stamping device 19 can form a plurality of axially spaced apart annular depressed portions or grooves on the outer periphery of the sleeve by radially inwardly pressing, with heating, the composite material drawn from the sleeve forming step, whereby the sleeve and the fibers are tightened together at the pressed portions. As a result, when the composite material is cut into chips at positions other than the pressed portions, the cut fibers are prevented from separating from each other or from the sleeve and are remained bound together. In accordance with the present invention, in addition to the blending device as described above, various types of fiber blending device conventionally used

as fiber blending device of this type may be conveniently employed for the present invention, and such device may include, for example, an air processor or the like.

The composite material according to the present invention may be used as a filament winding material or a pressurized molding material. In the case of the filament winding, the composite material according to the present invention is wound on a mandrel or a former, caused to be heated under pressures at temperatures higher than that of the thermoplastic resins by heating means so as to melt or fuse the thermoplastic resins of the sleeve and the thermoplastic fibers and then resolidified. Thereafter the mandrels and formers are then removed. The mandrels may become part of the molded products. In the case of the pressurized molding, the composite material may be placed on a mold, heated at temperatures higher than the melting point of the thermoplastic resin under pressures to melt the thermoplastic resin and the reinforcing fiber integrally thereto, and then resolidified. Thereafter the composite material may be molded in molded articles.

By using the composite material according to the present invention, there may be produced a solid molded article in which the reinforcing fiber is dispersed to a sufficient degree. It permits the easy production of products of complex dimensional shapes and of a small radius of curvature.

The composite material according to the present invention may be molded by molding means such as the filament winding method and the pressurized molding method into structural parts for automobiles, tennis racket frames, hockey sticks, skiing stocks, fishing rods, golf club shaft and so on. Furthermore, the composite material in the fiber form according to the present invention may be molded into mats in combination with other fibers by means of conventional weaving method.

The flexible composite material according to the present invention may be prepared by blending the thermoplastic resin fiber and the reinforcing fiber in arbitrary and quantitative blending ratios because, as described above, the blended fiber bundle composed of the thermoplastic resin fiber and the reinforcing fiber are used as a core material and a flexible sleeve made from the thermoplastic resin is provided around the core material. It further is practically valuable because it is superior in the post-processibility and flexibility, whereby molded articles with extremely high tensile strength and bending strength characteristics are given. The process for the preparation of the flexible composite material according to the present invention is also industrially favorable because it can reduce the number of steps and it requires the use of a simple apparatus.

The following examples will further illustrate the present invention.

#### 5 Example 1

A bundle and pellets of nylon 66 were prepared using a polymer prepared from hexamethylene diamine/adipic acid (HA salt) as a base material. The density of this nylon 66 was 1.14 g/cc, and the bundle was composed of 600 filaments of 3 denier each. Its tensile strength was 6.4 kg/mm<sup>2</sup>, and the elongation was 38 %. The reinforcing fiber to be blended with the nylon 66 fiber was a bundle of carbon fiber made from petroleum pitch. The carbon fiber bundle was composed of 6,000 filaments and had a density of 1.71 g/cc, a tensile strength of 310 kg/mm<sup>2</sup>, a tensile elastic modulus of  $22 \times 10^3$  kg/mm<sup>2</sup>, and an elongation of 1.4 %. The carbon bundle and the nylon 66 bundle wound on bobbins were continuously drawn through the fiber blending device 13 by the Nelson type feed roller 14 at a constant speed to obtain a blended fiber bundle composed of 64 % by volume of the carbon fiber and 36 % by volume of the nylon 66 fiber.

The fiber blending device 13 was composed of air nozzles and a fiber intermixing means. The two fibers supplied were each spread by blowing dry air from the nozzles, and the both spread fibers were passed through two small long fixed plates arranged in parallel with each other in the up-and-down positions to effect intermixing of the two fibers. During this step, a tension of about 30 grams was applied to the fibers using a sensor.

The blended fiber bundle thus formed was then transferred to a sleeve-covering device composed of the thermoplastic resin extruder 18 and a sleeve-covering cross head 16. During this step, the pellets of nylon 66 prepared above were supplied to the extruder 18 so as to form a sleeve around the blended fiber bundle, the product was then cooled by means of the cooling device 20 to get solidified, the product was drawn at a constant velocity by means of the Nelson type feed roller 11, and then it was wound by the winding apparatus 22. The extruder 18 was arranged to have a screw diameter of 20 mm and an extruding velocity of 0.34 liter/hour, and the temperature of the cross head die was set to be 281 °C and the drawing velocity of 10 m/minute.

The resulting sleeve surrounding the blended fiber bundle had an inner diameter of 5 mm, a thickness of 38 μm and a volume of 47% based on of the volume of the carbon fiber. The resultant



composite material was woven using a rapier loom to give a plain woven cloth of high quality without any fuzz caused and carbon fibers exposed on the surface thereof.

The composite material was also wound so as to be closely bound to become a thickness of about 6 mm on an aluminum alloy plate having a width of 200 mm and a thickness of 5 mm and then placed into a mold of a pressure molding apparatus. The mold was heated to 280 °C and kept for 5 minutes, and then given the pressure of 32 kg/cm<sup>2</sup> for 20 minutes. The mold was then cooled to ambient temperature while the pressure was kept applied. The resultant molded product was removed from the mold and cut into test pieces of 175 mm × 20 mm × 3 mm and 80 mm × 25 mm × 3 mm, respectively, so as to allow the carbon fibers to be positioned in the lengthwise direction. Using each 20 test pieces, the tensile and the bending tests were conducted. The average tensile strength for 20 test pieces was found to be 105.7 kg/mm<sup>2</sup> and the bending velocity was 91.4 kg/mm<sup>2</sup>.

#### Example 2

Test pieces were prepared by following Example 1 with the exception that the number of nylon 66 fiber filaments were 3,400 and the denier number per filament was 0.5. The test results were: tensile strength of 149.6 kg/mm<sup>2</sup> and bending strength of 131.3 kg/mm<sup>2</sup>. These figures are higher than those prepared in Example 1, and they show that more uniform composite material was given.

#### Example 3

A blended fiber bundle composed of 74 % by volume of carbon fiber and 26 % by volume of nylon 66 fiber was prepared by following Example 1 with the exception that the number of nylon 66 fiber filaments was changed to 370 and the denier number per filament was changed to 0.5. Using this blended filaments bundle, a composite material was prepared in the same manner as in Example 1 and test pieces were likewise given. The tensile strength was found to be 120.8 kg/mm<sup>2</sup> and the bending strength was 112.2 kg/mm<sup>2</sup>. The composite material was found to contain carbon fibers in higher content than that obtained in Example 1 and be superior to that of Example 1.

#### Example 4

A composite material was prepared in substantially the same manner as in Example 1 with the exception that the sleeve forming step was performed using the deairing pump 17 so as to closely bind the blended fiber bundle composed of the nylon 66 fiber and the carbon fiber. Test pieces were then likewise produced, and their tensile strength was found to be 138.4 kg/mm<sup>2</sup> and the bending strength of 130.1 kg/mm<sup>2</sup>. This shows that a porosity of the molded product was reduced.

#### Example 5

A composite material was prepared by following Example 1 with the exception that the tension before and after the fiber blending device 13 was changed to about 75 grams. This made it possible to set the extruding velocity at 2.04 liters/hour and the final drawing velocity at 60 meters/minute, leading to a remarkable increase in productivity. The tensile strength was found to be 104.9 kg/mm<sup>2</sup> and the bending strength was 91.8 kg/mm<sup>2</sup>.

#### Example 6

A composite material was prepared by following Example 1 with the exception that the carbon fiber bundle was surface treated by the sizing roller 25 and the blended fiber bundle by the sizing roller 15 and the tension before and after the fiber blending device was changed to about 50 grams. This permitted the extruding velocity to be set at 2.72 liters/hour and the final drawing velocity at 80 meters/minute, leading to a remarkable increase in producing speed. The tensile strength was found to be 109.2 kg/mm<sup>2</sup> and the bending strength was 90.3 kg/mm<sup>2</sup>.

#### Example 7

A composite material was prepared in substantially the same manner as in Example 1 with the exception that the sleeve was closely bonded to the blended fiber bundle composed of the nylon 66 fiber and the carbon fiber in which the sleeve forming step was performed under a reduced pressure using the deairing pump 17 and the composite material was provided with knots (annular grooves) at distances at every 10 mm by stamping at a temperature of about 280 °C and a pressure of about 70 Kg/cm<sup>2</sup> by means of the stamping device 19. The resulting composite material was chopped in the length of 50 mm. Substantially no separation



of fibers from the sleeve was observed. The chopped material was dispersed in random directions and laminated to give a composite material in the felt state having a thickness of 4.2 mm. This was heated at 270 °C using a far infrared heater and then inserted into a press mold that was operated under the pressure of 60 kg/cm<sup>2</sup>, leading to the production of composite products having a variety of curved surfaces.

#### Comparative Example 1

The blended fiber bundle prepared by the process of Example 1 was wound directly without passage through the sleeve covering device. This was subjected to plain weaving with a rapier loom, resulting in a woven cloth with a remarkable degree of fuzzes caused on the surface, and the cloth was found impractical. Test pieces were prepared in substantially the same manner as in Example 1 and subjected to tests. The results were: tensile strength of 74.2 kg/mm<sup>2</sup> and bending strength of 63.1 kg/mm<sup>2</sup>.

#### Claims

1. A flexible composite material comprising a core composed of a blend of a thermoplastic resin fiber and a reinforcing fiber, and a flexible sleeve formed of a thermoplastic resin and surrounding said core.

2. A flexible composite material according to claim 1, wherein said core is composed of from about 15 % to about 30 % by volume of the thermoplastic resin fiber and from about 85 % to about 70 % by volume of the reinforcing fiber, each based on the total fiber content.

3. A flexible composite material according to claim 1, wherein said thermoplastic resin fiber has a filament denier number in the range of about 0.03 to about 1.

4. A flexible composite material according to claim 1, wherein said reinforcing fiber has a filament denier number in the range of about 0.25 to about 1.

5. A flexible composite material according to claim 1, wherein said sleeve has a thickness in the range of from about 10 to about 200 μm.

6. A flexible composite material according to claim 1, wherein said sleeve is in close contact with the entire periphery of said core.

7. A flexible composite material according to claim 1, and being provided with a plurality of longitudinally equally spaced apart annular pressed portions on the outer periphery of said sleeve, each

annular pressed portion being formed by radially inwardly hot pressing the periphery of the sleeve so as to tighten the sleeve and the fibers together.

8. A flexible composite material according to claim 1, wherein said reinforcing fiber is a member selected from the group consisting of carbon fibers, glass fibers, polyamide fibers and mixtures thereof.

9. A process for preparing a flexible composite material, comprising providing a thermoplastic resin fiber and a reinforcing fiber, intimately blending said thermoplastic resin fiber and said reinforcing fiber, assembling said blended fibers to obtain a core, and extruding a thermoplastic resin over said core to form a thermoplastic resin sleeve surrounding said core.

10. A process according to claim 9, wherein said blending is carried out while applying a tension of at least about 2 g to each of said thermoplastic resin fiber and reinforcing fiber.

11. A process according to claim 9, further comprising treating said reinforcing fiber with a sizing agent before said blending step.

12. A process according to claim 9, further comprising treating said core with a sizing agent before said extruding step.

13. A process according to claim 9, wherein said extruding step is carried out while maintaining said core under vacuum so as to substantially reduce interstices between the blended fibers of said core and between said core and said sleeve.

14. A process according to claim 9, further comprising radially inwardly hot-pressing the sleeve after said extruding step to form a plurality of axially equally spaced apart annular depressed portions on the periphery of the sleeve so that the blended fibers and the sleeve are tightly bound at each depressed portion.

15. A process according to claim 14, further comprising cutting into chips the product obtained after said hot-pressing step at positions other than the depressed portions.

FIG. 1

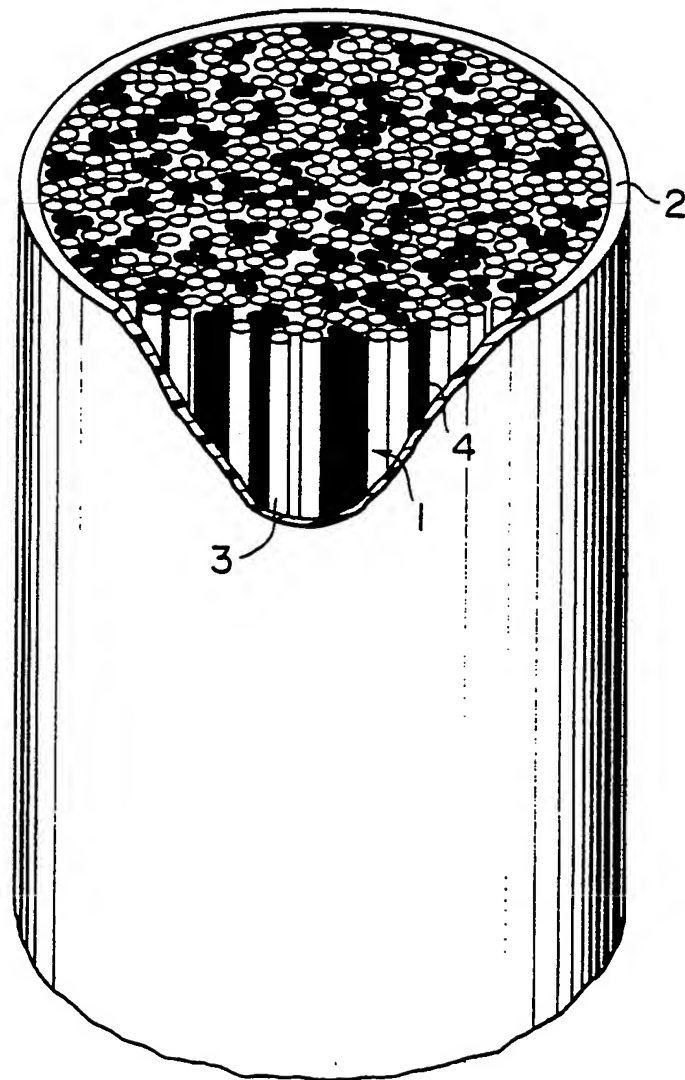
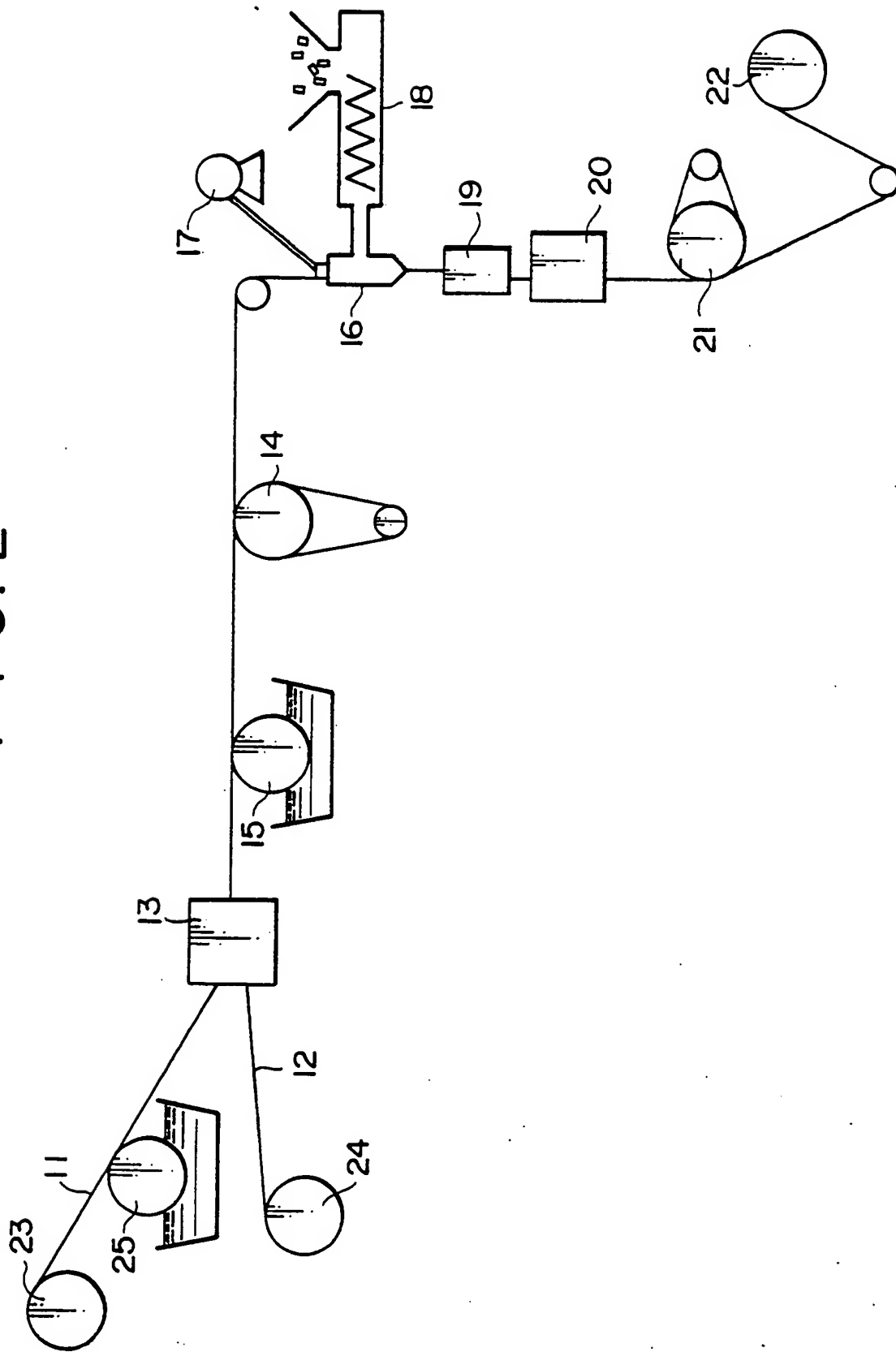


FIG. 2



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54 Flexible composite material and process for preparing same.

57 A flexible composite material comprising a core composed of a blend of a thermoplastic resin fiber (3) and a reinforcing fiber (4), and a flexible sleeve (2) formed of a thermoplastic resin and surrounding the core. The composite material may be prepared by intermixing a thermoplastic resin fiber (3) and a reinforcing fiber (4) to obtain a core, and then extruding a thermoplastic resin over the core.

FIG. 1



EP 0 226 420 A3



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| DOCUMENTS CONSIDERED TO BE RELEVANT  |   |  |   |
|--|---|--|---|
| Category   | Citation of document with indication, where appropriate, of relevant passages                             | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
| X  | FR-A-2 028 162 (BERKENHOFF UND DREBES AG)<br>* Page 2, line 19 - page 3, line 2;<br>page 3, lines 24-35 * | 1,6,8,9  | D 02 G 3/04<br>D 02 G 3/40                    |
| Y  | ---   | 11-13  |   |
| Y  | US-A-3 679 507 (A. MARZOCCHI)<br>* Column 3, lines 18-20 *  | 11,12  |   |
| Y  | US-A-3 773 449 (T.C. HAGER)<br>* Column 3, lines 64-68; column 4,<br>lines 36-44 *                        | 13   |   |
|  |   |  | TECHNICAL FIELDS SEARCHED (Int. Cl.4)         |
|  |   |  | D 02 G<br>B 29 C                              |
| The present search report has been drawn up for all claims   |   |  |   |
| Place of search<br>THE HAGUE   |   | Date of completion of the search<br>02-12-1987 | Examiner<br>HOEFER W.D.                       |
| <b>CATEGORY OF CITED DOCUMENTS</b><br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document<br>T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>I : document cited for other reasons<br>-----<br>& : member of the same patent family, corresponding document |   |  |   |